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Zinc Diphosphonates Templated by Organic Amines: Syntheses and Characterizations of $[NH_3(CH_2)_2NH_3]Zn(hedpH_2)_2 \cdot 2H_2O$ and $[NH_3(CH_2)_nNH_3]Zn_2(hedpH)_2 \cdot 2H_2O$ ($n = 4, 5, 6$) (hedp = 1-Hydroxyethylidenediphosphonate)

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Four new zinc diphosphonate compounds with formulas $[NH_3(CH_2)_2NH_3]Zn(hedpH_2)_2 \cdot 2H_2O$, **1**, $[NH_3(CH_2)_n NH_3]Zn_2(hedpH)_2 \cdot 2H_2O$, ($n = 4$, **2**; $n = 5$, **3**; $n = 6$, **4**) (hedp = 1-hydroxyethylidenediphosphonate) have been synthesized under hydrothermal conditions at 110 °C and in the presence of alkylenediamines $NH_2(CH_2)_nNH_2$ ($n = 2, 4, 5, 6$). Crystallographic data for **1**: monoclinic, space group $C2/c$, $a = 24.7422(15)$, $b = 5.2889(2)$, $c = 16.0338(2)$ Å, $\beta = 117.903(1)°$, $V = 1856.17(18)$ Å^3, $Z = 4$; **2**: monoclinic, space group $P2_1/n$, $a = 5.4970(3)$, $b = 12.1041(6)$, $c = 16.2814(12)$ Å, $\beta = 98.619(5)°$, $V = 1071.07(11)$ Å^3, $Z = 2$; **3**: monoclinic, space group $P2_1/n$, $a = 5.5251(2)$, $b = 12.5968(3)$, $c = 16.1705(5)$ Å, $\beta = 99.182(1)°$, $V = 1111.02(6)$ Å^3, $Z = 2$; **4**: triclinic, space group P-1, $a = 5.4785(2)$, $b = 14.1940(5)$, $c = 16.0682(6)$ Å, $\alpha = 81.982(2)°$, $\beta = 89.435(2)°$, $\gamma = 79.679(2)°$, $V = 1217.11(8)$ Å^3, $Z = 2$. In compound **1**, two of the phosphonate oxygens are protonated. The metal ions are bridged by the $hedpH_2^{2-}$ groups through three of the remaining four phosphonate oxygens, forming a one-dimensional infinite chain. The protonated ethylenediamines locate between the chains in the lattice. In compounds **2**−**4**, only one phosphonate oxygen is protonated. Compounds **2** and **3** have a similar three-dimensional open-network structure composed of $\{Zn_2(hedpH)_2\}_n$ double chains with strong hydrogen bonding interactions between them, thus generating channels along the [100] direction. The protonated diamines and water molecules reside in the channels. Compound **4** contains two types of $\{Zn_2(hedpH)_2\}_n$ double chains which are held together by strong hydrogen bonds, forming a two-dimensional network. The interlayer spaces are occupied by the $[NH_3(CH_2)_6NH_3]^{2+}$ cations and water molecules. The significant difference between structures **2**−**4** is also featured by the coordination geometries of the zinc atoms. The geometries of those in **2** can be described as distorted octahedral, and those in **3** as distorted square pyramidal. In **4**, two independent zinc atoms are found, each with a distorted octahedral and a tetrahedral geometry, respectively.

Introduction

In recent years, growing attention has been paid to the exploration of novel metal phosphonate compounds due to their potential applications in ion exchange, sorption, catalysis, etc.[1−4] The transition metal phosphonates are of interest because they are soluble in acid solution and, therefore, are more easily crystallized compared to those containing tetravalent metal ions.[5,6] A number of zinc phosphonate compounds have been prepared, most of which have been structurally determined either by single-crystal diffraction techniques or from X-ray powder diffraction data. These include monophosphonates $Zn(O_3PR) \cdot H_2O$ ($R = CH_3, C_2H_5, C_6H_5$),[7,8] diphosphonates $Zn_2[(O_3PC_2H_4PO_3)(H_2O)_2]$,[9] $Zn_2[(O_3PC_3H_6PO_3)]$,[9] $Zn(HO_3PC_3H_6PO_3H)$,[10] $Zn_3[(HO_3PC_3H_6PO_3)_2] \cdot 2H_2O$,[10] $Zn_2[(O_3PC_6H_4PO_3)(H_2O)_2]$,[11] $Zn_2[(O_3PC_{12}H_8PO_3)] \cdot 2H_2O$,[12] and $Zn[HO_3P(C_6H_4)_2PO_3H]$,[11] and functionalized phosphonates $Zn[O_3PCH_2P(O)(C_6H_5)_2]$,[13] $Zn[(O_3PCH_2P(O)(CH_3)(C_6H_5)] \cdot 0.67H_2O$,[13] $Zn(O_3PC_2H_4NH_2)$,[14] $Zn_3(O_3PC_2H_4CO_2)_2$, and $Zn(O_3PC_2H_4CO_2H) \cdot 1.5H_2O$.[15] The structures of these compounds range from one-dimensional chain, two-dimensional layer to three-dimensional pillared layer or open-framework. Factors which determine these structures include the length of the organic group in $R(PO_3)_2^{4-}$, the number of

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Table 1. Crystal Data and Structure Refinement for **1−4**

compound	**1**	**2**	**3**	**4**
empirical formula	$C_6H_{26}N_2O_{16}P_4Zn$	$C_8H_{28}N_2O_{16}P_4Zn_2$	$C_9H_{30}N_2O_{16}P_4Zn_2$	$C_{10}H_{30}N_2O_{16}P_4Zn_2$
formula weight	571.54	662.94	676.97	691.00
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$C2/c$	$P2_1/n$	$P2_1/n$	P-1
a Å	24.7422(15)	5.4970(3)	5.5251(2)	5.4785(2)
b Å	5.2889(2)	12.1041(6)	12.5968(3)	14.1940(5)
c Å	16.0338(2)	16.2814(12)	16.1705(5)	16.0682(6)
α °				81.982(2)
β °	117.903(1)	98.619(5)	99.182(1)	89.435(2)
γ °				79.679(2)
V Å^3	1856.17(18)	1071.07(11)	1111.02(6)	1217.11(8)
Z	4	2	2	2
D_{calc} g cm^{-3}	2.045	2.056	2.024	1.885
μ cm^{-1}	17.55	26.20	25.28	23.09
F(000)	1176	676	692	708
GOF on F^2	1.037	1.188	1.029	1.027
R1, wR2 [$I > 2\sigma(I)$]	0.0411, 0.0955	0.0296, 0.0877	0.0392, 0.0936	0.0372, 0.0866
(all data)	0.0612, 0.1037	0.0416, 0.0911	0.0585, 0.1013	0.0563, 0.0940
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ e Å^{-3}	0.776, −0.809	0.595, −0.525	0.714, −0.624	0.942, −0.634

potential binding sites of the functional group (X) in $O_3P{-}R{-}X$, and whether the phosphonate oxygens are protonated, etc. Due to our interest in studying the template influences on the structures of metal phosphonates based on 1-hydroxyethylidenediphosphonate [$CH_3C(OH)(PO_3)_2$, hedp],[16−18] herein we report four new zinc diphosphonates, namely [$NH_3(CH_2)_2NH_3$]Zn(hedpH_2)$_2$·2H_2O, **1**, [$NH_3(CH_2)_4NH_3$]Zn_2(hedpH)$_2$·2H_2O, **2**, [$NH_3(CH_2)_5NH_3$]Zn_2(hedpH)$_2$·2H_2O, **3**, and [$NH_3(CH_2)_6NH_3$]Zn_2(hedpH)$_2$·2H_2O, **4**.

Experimental Section

Materials and Methods. All the starting materials were reagent grade and used as purchased. The elemental analyses were performed on a PE 240C elemental analyzer. The infrared spectra were recorded on a IFS66V spectrometer with pressed KBr pellets. Thermal analyses were performed in nitrogen with a heating rate of 5 °C/min on a TGA-DTA V1.1B TA Inst 2100 instrument.

Synthesis of [$NH_3(CH_2)_2NH_3$]Zn(hedpH_2)$_2$·2H_2O, 1. A mixture of $ZnSO_4$·7H_2O (1 mmol, 0.2879 g), 50% hedpH_4 (2 cm^3), LiF (1 mmol, 0.0257 g), and H_2O (8 cm^3), adjusted by ethylenediamine to pH = 3 ∼ 4, was heated at 110 °C in a Teflon-lined stainless steel autoclave for 3 days. Colorless, needlelike crystals were collected as a monophasic product and judged by the powder XRD pattern. Yield: 57% based on Zn. Found (calcd.) for $C_6H_{26}N_2ZnO_{16}P_4$: C, 12.99(12.60); H, 4.66(4.55); N, 5.03(4.90). IR (KBr): 3563s, 3331s, 3160−2787(br), 1637m, 1607w, 1540m, 1490w, 1455w, 1412m, 1358w, 1344w, 1150s, 1080s, 1041s, 926s, 906s, 812m, 773w, 718w, 556m, 532w, 483w, 462w, 446w, 426w, 414w cm^{-1}.

Synthesis of [$NH_3(CH_2)_4NH_3$]Zn_2(hedpH)$_2$·2H_2O, 2. A mixture of $ZnCl_2$ (1 mmol, 0.1380 g), 50% hedpH_4 (1 cm^3), LiF (1 mmol, 0.0253 g), and H_2O (8 cm^3), adjusted by 1,4-butylenediamine to pH = 3 ∼ 4, was heated at 110 °C in a Teflon-lined stainless autoclave for 7 days. Colorless, needlelike crystals were discovered as a monophasic material and judged by powder XRD pattern. Yield: 75% based on Zn. Found (calcd.) for $C_8H_{28}N_2O_{16}P_4Zn_2$: C, 15.04 (14.48); H, 4.44 (4.22); N, 4.71 (4.22). IR (KBr): 3430m, 3086m(br), 1628m, 1539m, 1291w, 1160s, 1110s, 1006s, 905s, 796m, 567s, 501w, 469w cm^{-1}.

Synthesis of [$NH_3(CH_2)_5NH_3$]Zn_2(hedpH)$_2$·2H_2O, 3. A mixture of $ZnSO_4$·7H_2O (1 mmol, 0.2426 g), 50% hedpH_4 (1 cm^3), LiF (1 mmol, 0.0257 g), and H_2O (8 cm^3), adjusted by 1,5-pentamethylenediamine to pH = 3 ∼ 4, was heated at 110 °C in a Teflon-lined stainless autoclave for 7 days. Colorless, needlelike crystals were discovered as a monophasic material and judged by powder XRD pattern. Yield: 65% based on Zn. Found (calcd.) for $C_9H_{30}N_2O_{16}P_4Zn_2$: C, 15.35 (15.95); H, 4.66 (4.43); N, 4.62 (4.14). IR (KBr): 3457s, 3283m, 3045−2785(br), 1674m, 1626m, 1563m, 1529m, 1517m, 1478m, 1161s, 1098s, 1122s, 901s, 796s, 566s, 510w, 407m cm^{-1}.

Synthesis of [$NH_3(CH_2)_6NH_3$]Zn_2(hedpH)$_2$·2H_2O, 4. A mixture of $ZnCl_2$ (1 mmol, 0.1361 g), 50% hedpH_4 (1 cm^3), LiF (1 mmol, 0.0257 g), 1,6-hexamethylenediamine (3 mmol, 0.3482 g), and H_2O (8 cm^3) was heated at 110 °C in a Teflon-lined stainless autoclave for 7 days. Colorless, needlelike crystals were discovered as a monophasic material and judged by powder XRD pattern. Yield: 73% based on Zn. Found (calcd.) for $C_{10}H_{32}N_2O_{16}P_4Zn_2$: C, 18.43 (17.37); H, 4.87 (4.63); N, 4.49 (4.05). IR (KBr): 3434s, 3281−2790(br), 1684m, 1630m, 1547m, 1472w, 1420w, 1395w, 1370w, 1338w, 1156s, 1136s, 1112s, 1055s, 1004s, 936s, 903s, 807m, 734w, 665w, 585s, 566s, 523w, 478m, 457w, 425w, 412m cm^{-1}.

Single-Crystal X-ray Diffraction. Single crystals with dimensions 0.20 × 0.18 × 0.10 mm for **1**, 0.06 × 0.11 × 0.40 mm for **2**, 0.31 × 0.14 × 0.09 mm for **3**, and 0.36 × 0.13 × 0.08 mm for **4** were used for structural determinations on a Nonius CAD4 Mach3 (for **2**) or a Nonius KappaCCD (for **1**, **3**, **4**) diffractometer with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 293K. Intensity data were collected in the θ range of 3.48−30.04° for **1**, 2.11−27.95° for **2**, 3.48−32.02° for **3**, and 3.62−27.87° for **4**, using $\theta/2\theta$ mode. Number of measured and observed reflections [$I > 2\sigma(I)$] are 17793 and 2710 ($R_{int} = 0.0574$) for **1**, 2573 and 2200 ($R_{int} = 0.0175$) for **2**, 20022 and 3850 ($R_{int} = 0.0567$) for **3**, and 23456 and 5676 ($R_{int} = 0.0496$) for **4**. The data were reduced and corrected for Lp factors, decay, and absorptions ($T_{max,min}$: 0.846, 0.770 for **1**; 0.999, 0.947 for **2**; 0.798, 0.675 for **3**; and 0.834, 0.781 for **4**). The extinction corrections were applied.

The structures were solved by direct method and refined on F^2 by full-matrix least squares using SHELXTL.[19] All of the non-hydrogen atoms in the four compounds, except the carbon atoms in the disordered cations of [$NH_3(CH_2)_5NH_3$]$^{2+}$ in **3** and [$NH_3(CH_2)_6NH_3$]$^{2+}$ in **4**, were refined anisotropically. The C atoms in these cations were refined isotropically. All H atoms, except those in **2** and of water molecules, were placed in calculated positions. The H atoms of water molecules and those in **2** were located from the difference Fourier map and refined isotropically. Crystallographic data are summarized in Table 1. The selected bond lengths and angles are listed in Tables 2 −5 for **1−4**, respectively.

Results

Compounds **1−4** have been prepared under similar hydrothermal conditions. Both $ZnSO_4$ and $ZnCl_2$ can be used as the zinc sources leading to the same compound. The fluoride was added in order to improve the crystallization of the products.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Zn(1)−O(4)	2.0259(18)	Zn(1)−O(1)	2.1393(18)
Zn(1)−O(2B)	2.1538(18)	P(1)−O(2)	1.4988(18)
P(1)−O(1)	1.5093(18)	P(1)−O(3)	1.577(2)
P(2)−O(4)	1.5080(18)	P(2)−O(5)	1.5040(19)
P(2)−O(6)	1.5655(19)		
O(4A)−Zn(1)−O(4)	180.00(9)	O(4A)−Zn(1)−O(1)	88.37(7)
O(4)−Zn(1)−O(1)	91.63(7)	O(1)−Zn(1)−O(1A)	180.00(9)
O(4)−Zn(1)−O(2B)	89.33(7)	O(1)−Zn(1)−O(2B)	91.60(7)
O(4)−Zn(1)−O(2C)	90.67(7)	O(1)−Zn(1)−O(2C)	88.40(7)
O(2B)−Zn(1)−O(2C)	180.00(7)	P(1)−O(1)−Zn(1)	134.97(11)
P(1)−O(2)−Zn(1D)	139.29(11)	P(2)−O(4)−Zn(1)	134.73(11)

Symmetry transformations used to generate equivalent atoms; A: $-x, -y + 1, -z$; B: $x, y - 1, z$; C: $-x, -y + 2, -z$; D: $x, y + 1, z$.

Table 3. Selectec Bond Lengths (Å) and Angles (deg) for **2**

Zn(1)−O(1A)	2.0051(19)	Zn(1)−O(2B)	2.0083(19)
Zn(1)−O(4)	2.0535(18)	Zn(1)−O(5B)	2.064(2)
Zn(1)−O(7)	2.278(2)	Zn(1)−O(1)	2.479(2)
P(1)−O(1)	1.5112(19)	P(1)−O(2)	1.505(2)
P(1)−O(3)	1.549(2)	P(1)−C(1)	1.836(3)
P(2)−O(5)	1.509(2)	P(2)−O(4)	1.5206(18)
P(2)−O(6)	1.535(2)		
O(1A)−Zn(1)−O(2B)	100.06(8)	O(1A)−Zn(1)−O(4)	90.29(8)
O(2B)−Zn(1)−O(4)	164.16(8)	O(1A)−Zn(1)−O(5B)	105.93(8)
O(2B)−Zn(1)−O(5B)	93.85(8)	O(4)−Zn(1)−O(5B)	94.80(8)
O(1A)−Zn(1)−O(7)	151.98(8)	O(2B)−Zn(1)−O(7)	86.05(8)
O(4)−Zn(1)−O(7)	79.30(7)	O(5B)−Zn(1)−O(7)	100.86(8)
O(1A)−Zn(1)−O(1)	77.78(8)	O(2B)−Zn(1)−O(1)	89.99(7)
O(4)−Zn(1)−O(1)	80.44(7)	O(5B)−Zn(1)−O(1)	174.07(7)
O(7)−Zn(1)−O(1)	74.88(7)	P(1)−O(1)−Zn(1A)	139.52(13)
P(1)−O(1)−Zn(1)	113.81(10)	Zn(1A)−O(1)−Zn(1)	102.22(8)
P(1)−O(2)−Zn(1C)	131.68(12)	P(2)−O(4)−Zn(1)	120.00(11)
P(2)−O(5)−Zn(1C)	134.65(12)	C(1)−O(7)−Zn(1)	107.27(15)

Symmetry transformations used to generate equivalent atoms; A: $-x + 1, -y + 1, -z + 1$; B: $x - 1, y, z$; C: $x + 1, y, z$.

Table 4. Selectec Bond Lengths (Å) and Angles (deg) for **3**

Zn(1)−O(5A)	1.9991(18)	Zn(1)−O(4)	2.0103(17)
Zn(1)−O(2B)	2.0285(16)	Zn(1)−O(1)	2.0578(18)
Zn(1)−O(7B)	2.3165(19)	P(1)−O(1)	1.5101(18)
P(1)−O(2)	1.5223(17)	P(1)−O(3)	1.5341(19)
P(2)−O(4)	1.5102(18)	P(2)−O(5)	1.5162(17)
P(2)−O(6)	1.5511(18)		
O(5A)−Zn(1)−O(4)	98.51(7)	O(5A)−Zn(1)−O(2B)	92.21(7)
O(4)−Zn(1)−O(2B)	161.96(7)	O(5A)−Zn(1)−O(1)	107.95(8)
O(4)−Zn(1)−O(1)	93.78(7)	O(2B)−Zn(1)−O(1)	96.68(7)
O(5A)−Zn(1)−O(7B)	149.28(7)	O(4)−Zn(1)−O(7B)	84.67(7)
O(2B)−Zn(1)−O(7B)	78.78(6)	O(1)−Zn(1)−O(7B)	102.28(7)
P(1)−O(1)−Zn(1)	135.19(11)	P(1)−O(2)−Zn(1C)	121.81(10)
P(2)−O(4)−Zn(1)	131.75(10)	P(2)−O(5)−Zn(1A)	139.59(12)
C(1)−O(7)−Zn(1C)	107.28(14)		

Symmetry transformations used to generate equivalent atoms; A: $-x + 1, -y + 1, -z$; B: $x - 1, y, z$; C: $x + 1, y, z$.

Same compound can be obtained without the presence of LiF. The infrared spectra of all compounds show a series of bands in the 1000−1200 cm^{-1} region, which are attributed to the stretching vibrations of phosphonate PO_3 groups. The broad bands around 3000 cm^{-1}, arising from the O−H stretching vibrations of H_2O, hydroxy group, and the protonated phosphonate oxygens, suggest the extensive hydrogen bonds present in all four compounds.

Description of Structure 1. Compound **1** crystallizes in space group *C*2/*c*. The structure consists of one Zn atom, two equivalent $hedpH_2^{2-}$ groups, and one protonated ethylenediamine cation. The Zn atom sits at a special position. The other atoms occupy general positions. The geometry around the Zn atom can be described as a distorted octahedron. All six binding sites are provided by phosphonate oxygens. The Zn−O bond lengths range from 2.026(2) to 2.154(2) Å, which are close to those in $Zn(C_6H_5PO_3)\cdot H_2O$ [mean 2.14(1) Å].[7] The O−Zn−O bond angles are within 2° deviation from their ideal values. The $hedpH_2^{2-}$ ligand, with singly protonated phosphonate groups at either end, has only four phosphonate oxygens for coordination to zinc atoms, three of which [O(1), O(4), O(2)] bridge the Zn atoms in a chelating bridging mode, forming infinite chains along [010] direction (Figure 1). The remaining one [O(5)] is pendant, and it is involved in the hydrogen bonding network. The P−O(H) distances [1.577(2), 1.566(2) Å] are significantly longer than those of P−O(Zn) [1.499(2)−1.509(2) Å] and P═O [1.504(2) Å]. The protonated ethylenediamine and water molecules fill the spaces between the chains (Figure 2), forming extensive hydrogen bonds in the lattice. The shortest contact is 2.641(3) Å between O(3) and O(1w).

Table 5. Selectec Bond Lengths (Å) and Angles (deg) for **4**

Zn(1)−O(2A)	2.005(2)	Zn(1)−O(1B)	2.014(2)
Zn(1)−O(4)	2.064(2)	Zn(1)−O(5A)	2.077(2)
Zn(1)−O(7)	2.292(2)	Zn(1)−O(1)	2.394(2)
Zn(2)−O(12C)	1.908(2)	Zn(2)−O(9A)	1.917(2)
Zn(2)−O(11)	1.935(2)	Zn(2)−O(8)	1.976(2)
P(1)−O(2)	1.510(2)	P(1)−O(1)	1.521(2)
P(1)−O(3)	1.537(2)	P(2)−O(4)	1.511(2)
P(2)−O(5)	1.507(2)	P(2)−O(6)	1.566(2)
P(3)−O(9)	1.501(2)	P(3)−O(8)	1.518(2)
P(3)−O(10)	1.550(2)	P(4)−O(13)	1.509(2)
P(4)−O(11)	1.521(2)	P(4)−O(12)	1.530(2)
O(2A)−Zn(1)−O(1B)	99.94(9)	O(2A)−Zn(1)−O(4)	165.40(9)
O(1B)−Zn(1)−O(4)	90.29(8)	O(2A)−Zn(1)−O(5A)	93.34(8)
O(1B)−Zn(1)−O(5A)	106.85(9)	O(4)−Zn(1)−O(5A)	93.61(8)
O(2A)−Zn(1)−O(7)	87.71(9)	O(1B)−Zn(1)−O(7)	153.89(8)
O(4)−Zn(1)−O(7)	78.67(8)	O(5A)−Zn(1)−O(7)	97.49(8)
O(2A)−Zn(1)−O(1)	90.63(8)	O(1B)−Zn(1)−O(1)	78.95(8)
O(4)−Zn(1)−O(1)	81.09(8)	O(5A)−Zn(1)−O(1)	172.26(8)
O(7)−Zn(1)−O(1)	76.02(7)	O(12C)−Zn(2)−O(9A)	102.75(10)
O(12C)−Zn(2)−O(11)	117.33(10)	O(9A)−Zn(2)−O(11)	109.99(10)
O(12C)−Zn(2)−O(8)	115.50(10)	O(9A)−Zn(2)−O(8)	110.91(9)
O(11)−Zn(2)−O(8)	100.54(9)	P(1)−O(1)−Zn(1B)	139.08(13)
P(1)−O(1)−Zn(1)	115.00(11)	Zn(1B)−O(1)−Zn(1)	101.05(8)
P(1)−O(2)−Zn(1D)	133.30(13)	P(2)−O(4)−Zn(1)	120.12(12)
P(2)−O(5)−Zn(1D)	133.70(13)	C(1)−O(7)−Zn(1)	106.42(16)
P(3)−O(8)−Zn(2)	125.61(13)	P(3)−O(9)−Zn(2D)	145.67(15)
P(4)−O(11)−Zn(2)	129.68(14)	P(4)−O(12)−Zn(2C)	134.10(14)

Symmetry transformations used to generate equivalent atoms; A: $x + 1, y, z$; B: $-x + 3, -y + 2, -z$; C: $-x + 3, -y + 1, -z + 1$; D: $x - 1, y, z$.

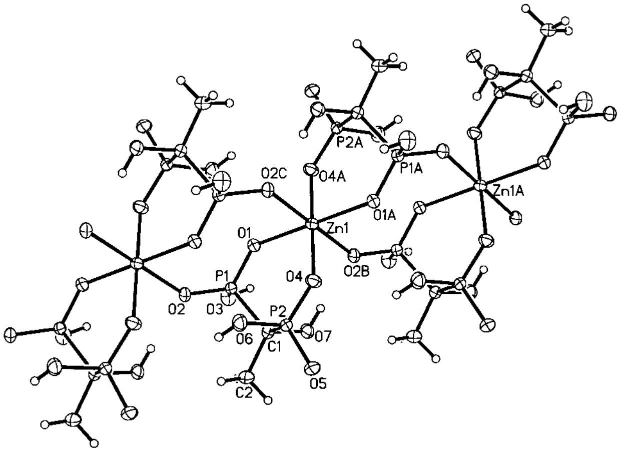

Figure 1. A fragment of the single chain in **1** with atomic labeling scheme (50% probability).

Description of Structure 2. Compound **2** crystallizes in space group *P*2$_1$/*n*. In this case, only one phosphonate oxygen of hedp is protonated. Consequently, the zinc atom replaces the second proton in compound **1**, leading to the compound **2**, where a

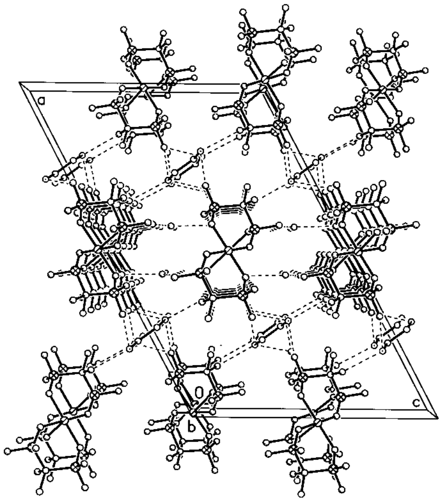

Figure 2. Structure **1** packed along [010] direction. All H atoms are omitted for clarity.

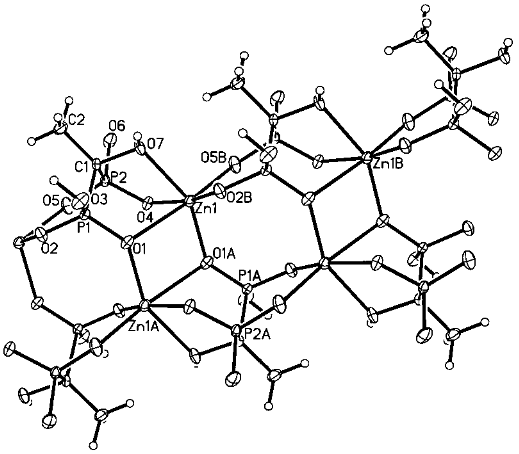

Figure 3. A fragment of the double chain in **2** with atomic labeling scheme (50% probability).

$\{Zn_2(hedpH)_2\}_n$ double chain is constructed (Figure 3). The double chain is composed of two {Zn(hedpH)} single chains which are connected to each other by edge-sharing of ZnO_6 octahedra. Within the single chain, the Zn atoms are bridged by $hedpH^{3-}$ groups in a bis(chelating) mode using four phosphonate oxygens O(1), O(2), O(4), and O(5). The O(7) atom from the hydroxy group also takes part in the binding. The sixth binding site of each Zn, occupied by O(1), is shared with the $\{ZnO_6\}$ octahedron from the other single chain. An inversion center sits in the middle of this sharing edge (Figure 3). The average Zn−O bond length [2.148(2) Å] is in agreement with that of $Zn(C_6H_5PO_3)\cdot H_2O$ [mean 2.14(1) Å],[7] although the Zn(1)−O(2) distance [2.479(2) Å] is significantly longer. A long Zn−O bond length is also observed in $Zn_2[(O_3PC_2H_4PO_3)(H_2O)_2]$ [2.468(7) Å][9] and $Zn_2(O_3PC_{12}H_8PO_3)\cdot 2H_2O$ [2.441(10) Å].[12] The O−Zn(1)−O bond angles are in the range 74.88(7)−174.07(7)°.

Two phosphonate oxygens [O(3), O(6)] of the $hedpH^{3-}$ group are not coordinated to the zinc ion; one of the phosphonate oxygens [O(3)] is protonated. The P−O(3) [1.549 (2) Å] and P−O(6) [1.535(2) Å] distances lie between the P−O(H) [1.577(2), 1.566(2) Å] and P=O [1.504(2) Å] distances, as observed in compound **1**. These two oxygens from adjacent double chains form very strong hydrogen bonds [$O(3)\cdots O(6)^i$ = 2.428(3) Å, symmetry code: *i*, $-x + 3/2$, $y - 1/2$, $-z + 1/2$], thus forming a three-dimensional open-network structure with channels along the [100] direction (Figure 4). The same phenomenon has been observed in $[NH_3(CH_2)_4NH_3]Fe_2(hedpH)_2\cdot 2H_2O$.[20] The $[NH_3(CH_2)_4NH_3]^{2+}$ cations and water molecules reside in the channels, with extensive hydrogen bonding interactions.

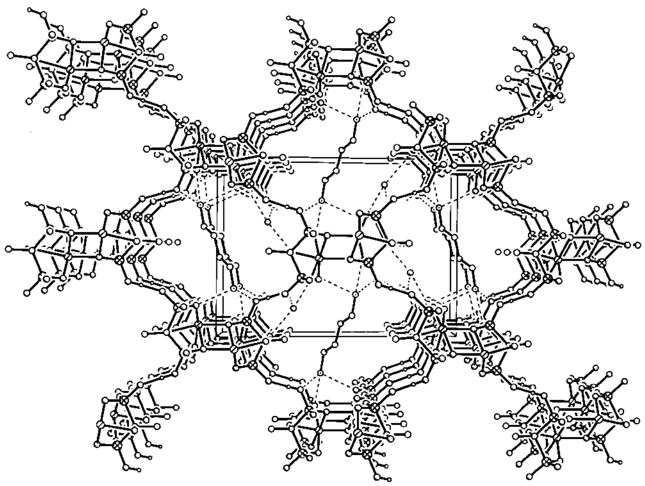

Figure 4. Structure **2** packed along [100] direction. All H atoms except H(3) are omitted for clarity.

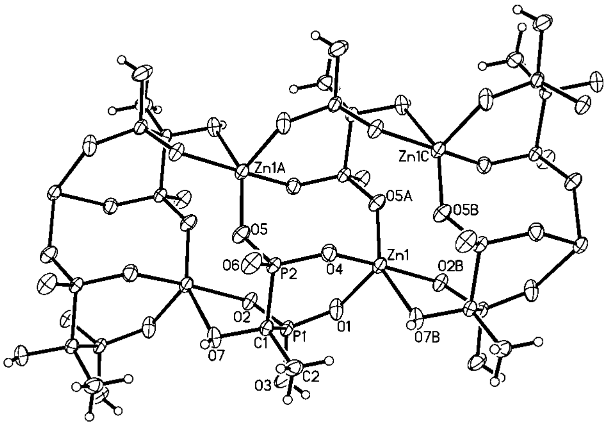

Figure 5. A fragment of the double chain in **3** with atomic labeling scheme (50% probability).

Description of Structure 3. Compound **3** also crystallizes in space group $P2_1/n$, and it's isostructural to compound **2**. It contains infinite double chains of $\{Zn_2(hedpH)_2\}_n$ (Figure 5), which are further linked to each other through very strong hydrogen bonds. The $O(3)\cdots O(6)^i$ (symmetry code: $3/2 - x$, $1/2 + y$, $1/2 - z$) distance in this case is 2.434 Å. One-dimensional channels are again generated which host the $NH_3(CH_2)_5NH_3^{2+}$ cations and H_2O molecules (Figure 6). The $NH_3(CH_2)_5NH_3^{2+}$ cations, however, are heavily disordered. The structural differences between **2** and **3** are recognized not only by the organic counterions, where the 1,5-pentamethylenediammonium in **3** replaces 1,4-butylenediammonium in **2**, but also by the coordination geometries around the zinc atoms. The Zn atom in **2** is six coordinated, with a distorted octahedral environment, whereas it is five coordinated in **3**, with a distorted square-pyramidal geometry. The $Zn(1)\cdots O(5B)$ distance [2.573 Å] is too long to be considered a coordination bond.

Description of Structure 4. Compound **4** crystallizes in space group *P*-1. All the atoms in this structure occupy general positions. The structure contains two types of double chains

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(20) Zheng, L.-M.; Song, H.-H.; Lin, C.-H.; Wang, S.-L.; Hu, Z.; Yu, Z.; Xin, X.-Q. *Inorg. Chem.* **1999**, *38*, 4618.

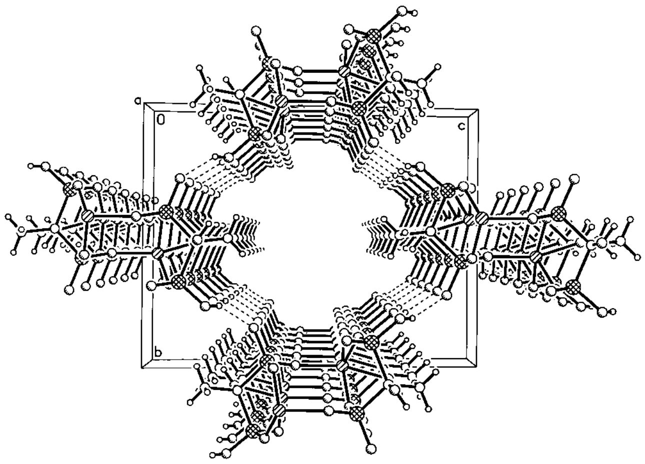

Figure 6. Structure **3** packed along [100] direction. All H atoms except H(3) and the disordered $[NH_3(CH_2)_5NH_3]^{2+}$ cations are omitted for clearity.

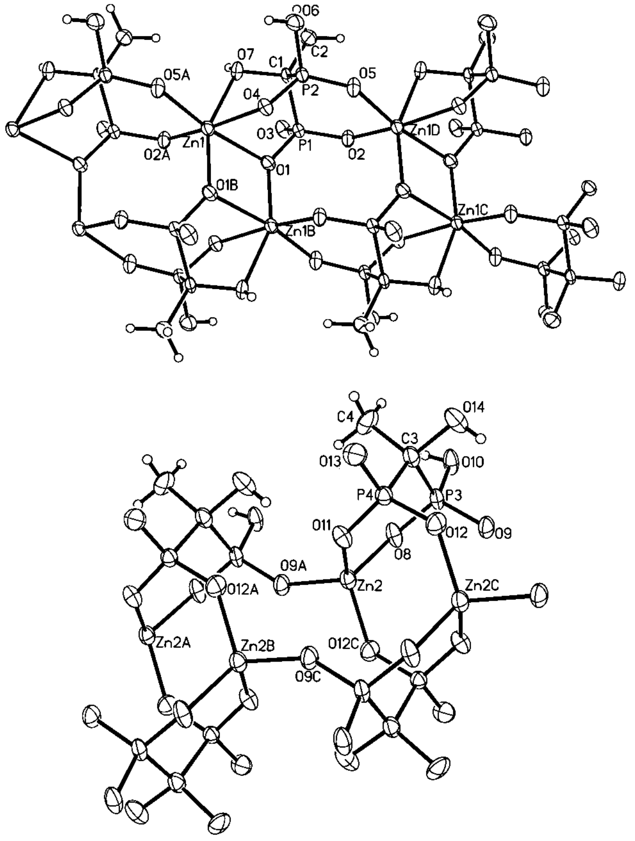

Figure 7. A fragment of the double chain (I) (a) and the double chain (II) (b) in **4** with atomic labeling scheme (50% probability).

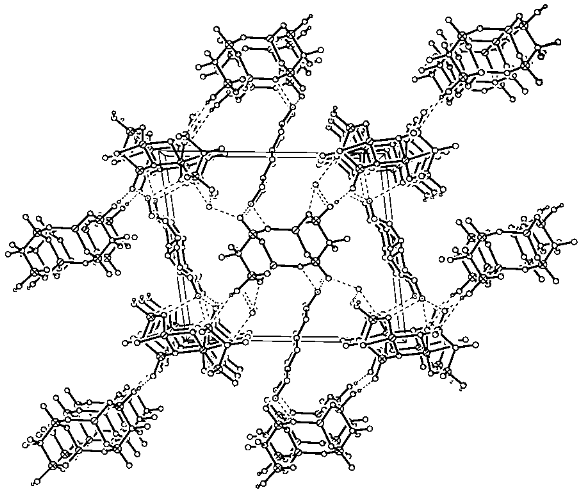

Figure 8. Structure **4** packed along [100] direction. All H atoms except H(6) and H(10) are omitted for clearity.

with the same formula, $\{Zn_2(hedpH)_2\}_n$. Subsequently, two independent zinc atoms are crystallographically distinguished, each belongs to one type of double chain.

The structure of chain (I) is reminiscent of the double chain in **2**. The monoprotonated $hedpH^{3-}$ group serves as a bis(chelating) ligand and bridges the Zn(1) atoms into an infinite single chain. Two such single chains are fused together through edge-sharing of ZnO_6 octahedra, forming an infinite double chain as shown in Figure 7a. The coordination geometry around the Zn(1) atom is distorted octahedral. The Zn(1)−O bond lengths fall in the range 2.005(2)−2.394(2) Å, in agreement with those in **2**. The structure of chain (II) is unique compared to those in compounds **1**−**3**. In this chain, the Zn(2) atom is four-coordinated with a distorted tetrahedral geometry (Figure 7b). The Zn(2)−O bond lengths are between 1.908(2) and 1.976(2) Å. The O−Zn(2)−O bond angles [100.54(9)−117.33(10)°] are deviated from their regular values within 9°. Each $hedpH^{3-}$ ligand is coordinated to three equivalent Zn(2) atoms, using four phosphonate oxygens O(8), O(9), O(11), and O(12). One of the remaining two phosphonate oxygens, O(10), is protonated. The P(3)−O(10) bond distance [1.550(2) Å] is much longer than that of the pendant P(4)−O(13) [1.509(2) Å].

These two chains [(I) and (II)] are arranged in the lattice alternatively. A very strong hydrogen bond between O(3) from chain (I) and O(10) from chain (II) connects the two chains into a layer. The O(3)···O(10) distance is 2.440 Å. Direct interactions between the layers are weak. The shortest O(6)···O(13^i) distance between the layers is 4.035 Å (symmetry code: i, $x - 1$, $y + 1$, z). These layers are held together through hydrogen bond interactions with the O(2w) atom from the lattice water, forming extensive network which contains cavities (Figure 8). The O2w···O(6^{ii}) and O(2w)···O(13^{iii}) distances are 2.533 and 2.674 Å, respectively (symmetry code: ii, $x - 1$, $y - 1$, z; iii, $x - 1$, y, z). The 1,6-hexamethylenediammonium cations fill the spaces of these cavities, and they are stabilized by the extensive hydrogen bonds with the anionic network.

Thermal Analyses. Thermogravimetric analyses reveal three steps of decomposition for all compounds. In the first step, the observed weight losses at 200 °C are 6.6% for **1**, 5.7% for **2**, 5.3% for **3**, and 5.3% for **4**, respectively, close to the theoretical values for the removal of two molecules of water [6.3% for **1**, 5.4% for **2**, 5.3% for **3**, and 5.2% for **4**]. For compound **1**, a second step decomposition follows right after the dehydration at about 200 °C. The compounds **2**−**4**, however, are stable until about 300 °C. The second decomposition stage, mainly attributed to the release of organic amines, is incomplete and is followed immediately by the third step of decomposition, with the collapse of the crystal lattice.

Discussion

The structures of compounds **1**−**4** are different from the other zinc diphosphonates reported so far. For those concerned with fully deprotonated $O_3P-R-PO_3$ ($R = C_2H_4$, C_3H_6, C_6H_4, $C_{10}H_8$) ligands, pillared layered structures are usually found.[9−12] The interlayer separations vary with the size of cross-linking organic groups. When one or two phosphonate oxygens are protonated, such as in compounds $Zn_3[(HO_3PC_3H_6PO_3)_2(H_2O)_2]$, $Zn(HO_3PC_3H_6PO_3H)$,[10] and $Zn(HO_3PC_{12}H_8PO_3H)$,[11] double chains with alternating Zn and P atoms are obtained. Consequently, compound $Zn_3[(HO_3PC_3H_6PO_3)_2(H_2O)_2]$ shows a three-dimensional structure with large elliptical pores. Compounds $Zn(HO_3PC_3H_6PO_3H)$ and $Zn(HO_3PC_{12}H_8PO_3H)$ have a layer structure built up from inorganic double chains and organic crosslinkers. In compounds **1**−**4**, single chain or double chain structures are observed. The arrangement of the double chains in **2**−**4** are also distinguished from those in $Zn(HO_3PC_3H_6PO_3H)$ and $Zn(HO_3PC_{12}H_8PO_3H)$. In the latter compounds, each $\{CPO_3\}$ group of the diphosphonate is involved in a separate double chain. In **2**−**4**, however, both $\{CPO_3\}$ groups of hedp participate in the construction of the same double chain, $\{Zn_2(hedpH)_2\}_n$. Obviously, these structural differences can be caused by the nature of the hedp ligand used in the present cases, which has a shorter length organic group, and the counterions involved. Like methylenediphosphonate,[21] hedp favors the formation of stable M−O−P−C−P−O six-membered rings with metal ions. In the four compounds reported here, the protonated hedp behaves as a chelating bridging ligand using three or four of its phosphonate oxygens. The doubly protonated $hedpH_2^{2-}$ ligand forms a linear single chain of $\{Zn(hedpH_2)_2\}_n$ with the zinc ions, as described in **1**. The singly protonated $hedpH^{3-}$ ligand, on the other hand, forms $\{Zn_2(hedpH)_2\}_n$ double chains with the zinc ions, as found in **2**−**4**. In the zinc compounds $Zn[O_3PCH_2P(O)(C_6H_5)_2]$ and $Zn[(O_3PCH_2P(O)(CH_3)(C_6H_5)]\cdot 0.67H_2O$,[13] where the two phosphorus atoms are separated by a single methyl group, the M−O−P−C−P−O six-membered rings are also formed, though their structures are affected by the geometry and steric bulk of the organic precusors in a different way.

The structural differences among compounds **1**−**4** are mainly attributed to the templates employed. The template $NH_2(CH_2)_2NH_2$ with a smaller size directs the formation of a linear single chain compound **1**. The templates $NH_2(CH_2)_nNH_2$ ($n = 4, 5, 6$) with a larger size direct the formation of anionic double chains, as in compounds **2**−**4**. These double chains are, in turn, held together by strong hydrogen bonds, forming three-dimensional open-networks as seen in **2**−**3**. The one-dimensional channels thus generated host the protonated organic diamines and water molecules. It is interesting to note that the interchain hydrogen bonds in **3** are almost as strong as those in **2**, though the protonated 1,5-pentamethylenediamine is heavily disordered to fit into the channel. Further, the involvement of 1,6-hexamethylenediammonium in **4** destroys the interchain hydrogen bonds in one direction. Therefore, only a two-dimensional anionic network is observed in compound **4**.

For compounds **2**−**4**, all three contain similar $\{Zn_2(hedpH)_2\}$ double chains. The coordination geometries around the zinc atoms, however, differ remarkably. In **2**, the zinc atom has a distorted octahedral environment, while it has a distorted square-pyramidal environment in **3**. In compound **4**, the tetrahedral geometry is observed for the Zn atoms, as is the octahedral geometry. This result reflects, on one hand, the versatile coordination abilities of the zinc atom. On the other hand, the size of the organic diammonium has apparent influences on the anionic networks and, hence, the environment around the zinc atoms. It has to be noted that only the tetrahedral arrangement of Zn has been observed in the other zinc phosphonates reported so far which involve one or two protonated phosphonate oxygens. Further, a five-coordinated Zn atom in a zinc phosphonate has not yet been reported.

The four structures **1**−**4** can be related to those of the other transition metal−hedp compounds templated by organic amines. Compound **1** is isostructural to the nickel compound $[NH_3(CH_2)_2NH_3][Ni(hedpH_2)_2]\cdot 2H_2O$,[17] but is different from the copper compound $[NH_3(CH_2)_2NH_3]_2Cu_2(hedp)_2\cdot H_2O$[22] with the same template. Compound **2** is isostructural to the iron compound $[NH_3(CH_2)_4NH_3][Fe_2(hedpH)_2]\cdot 2H_2O$[20] instead of the mononuclear nickel compound $[NH_3(CH_2)_4NH_3][Ni(hedpH_2)_2(H_2O)_2]$[17] templated by 1,4-butylenediamine. Interestingly, an entirely new structure type of metal−hedp compounds is discovered in **4**, where two different double chains are involved in the same structure. Further work is in progress in order to understand the template influences on directing the structures of metal phosphonates.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the four compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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